

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.651.2-183.2

MOLDING CORDIERITE-BASED POROUS CERAMIC OF A COMPLEX PROFILE

V. Yu. Prokof'ev,¹ A. V. Kunin,¹ and A. P. Il'in¹Translated from *Steklo i Keramika*, No. 9, pp. 14–17, September, 2004.

It is demonstrated that pastes obtained from cordierite milled jointly with a surfactant are suitable for extruding porous ceramics of a complex profile. The suspensions consisting of the components for the synthesis of cordierite have unsatisfactory molding properties. The processes of high-temperature calcination of molded cordierite ceramics are studied.

One of the properties of cordierite $2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ responsible for its wide application is its low TCLE ($8 \times 10^{-6} \text{ K}^{-1}$). This is very important when the material has to serve under abrupt temperature fluctuations. The resistance of cordierite to thermal shocks, as well as its relatively low cost have provoked an interest in this material on the part of numerous researchers. Cordierite has found wide application in the technology of catalysts, in particular, cellular block catalysts [1–3].

Industrial cordierite is produced by high-temperature calcination of respective mixtures for 20–40 h [1]. The phase transformations in this process are thoroughly studied as well, for instance, in [1, 2, 4, 5]. To accelerate thermal synthesis or to decrease the temperature of synthesis, some authors have proposed to use preliminary mechanochemical activation of the initial batch [2, 3, 5]. The temperature of synthesis needs to be lowered in the cases of producing a porous material, for instance, a catalyst carrier [2, 3].

Another very complicated stage of producing articles with preset parameters and configuration is molding. Molding is performed by the extrusion method whose advantages include a high efficiency, an easy transition from one standard size to another, etc. Extrusion molding pastes have a high (sometimes up to 90%)² content of the solid phase, therefore the interaction between the dispersed and the dispersion phases has a crucial effect on the moldability of pastes. It was earlier shown that not all pastes are suitable for extrusion, and the more complicated is the shape of the extrudate, the stricter requirements are imposed on the properties of the molding system [6, 7].

Of special interest is the production of articles by extruding pastes consisting of initial material for cordierite and then firing them, when the required compound is actually synthesized. In this case it is necessary to study such important aspect as the molding properties of pastes. Furthermore, there are important issues of regulating the structural-mechanical and flow properties³ of pastes based on ready cordierite, since the data on these issues in the literature are scarce and the optimum formulas are selected empirically by the trial-and-error method.

The following initial components were used for the production of porous cordierite ceramics:

I) kaolinite $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, talc $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$, and hydrargillite $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$;

II) $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$;

III) cordierite $2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ and dry polyvinyl alcohol (PVA).

All components in mixtures I and II were taken in a stoichiometric ratio corresponding to the reaction of the synthesis of cordierite. The choice of these compounds is justified in [3].

All mixtures were milled in a VM-4 roll-ring vibration mill with a vibration frequency of 930 min^{-1} and power intensity 5.4 kW/kg . The milling duration was 1 h. After milling mixtures I and II were mixed with 5% aqueous PVA solution and mixture III was mixed with water. The optimum molding moisture was monitored on a conical plastometer designed by P. A. Rebinder with the cone immersed according to the recommendations in [9]. After molding, cylindrical

¹ Ivanovo State Chemical Engineering University, Ivanovo, Russia.

² Here and elsewhere in wt. %.

³ We have introduced an arbitrary division into structural-mechanical and flow properties for the convenience of discussion. This is discussed in more detail in [8].

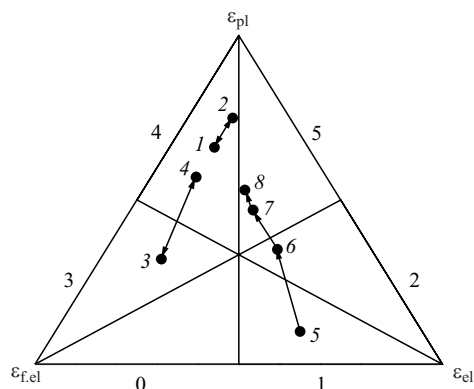


Fig. 1. Diagrams of the evolution of elastic ε_{el} , fast elastic $\varepsilon_{f,el}$, and plastic deformations ε_{pl} in pastes based on cordierite, kaolinite, talc, and hydrargillite; $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$: 1, 2) kaolinite, talc, hydrargillite + 5% surfactant solution (I); 3, 4) $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ + 5% surfactant (II); 5 – 8) cordierite + dry PVA (III). Preliminary mechanical activation of components: 1, 3) separate, 2, 4 – 8) joint. Quantity of PVA: 5) 1%, 6) 3%, 7) 5%, 8) 7%.

articles were sun-dried in air and then dried at a temperature of 60 – 80°C. Next, the samples were calcined at various temperatures for 1 h.

The structural-mechanical properties of the pastes were studied using a plastometer designed by D. M. Tolstoi according to the method described in [10]. The paste flow curves were obtained with a Rheotest-2 rotation viscosimeter in the shear velocity interval of 5 – 5000 sec^{-1} . The flow properties were calculated based on complete rheological curves [6, 8]. The mechanical strength in face crushing and the pore volume were determined using the standard methods [11].

Since the initial material for the synthesis of cordierite has sufficiently large particle size, for successful extrusion and high-temperature synthesis it has to be preliminary crushed. The milling of initial components can be performed separately or jointly. The research performed by us and by

E. G. Avvakumov with colleagues demonstrated the advantages of joint milling for the subsequent stage of cordierite synthesis [1 – 3].

A paste prepared from a mixture where all components are milled separately has clearly expressed plastic properties, which is corroborated by the paste classified as structural-mechanical type 4 (Fig. 1). Its slow elastic deformation are weakly expressed. The paste has a relatively short relaxation period (600 sec) and a low-strength coagulation structure, which is evidenced by the power consumed in destroying the coagulation structure equal to 2.5 MW/m^3 (Table 1).

The use of joint milling of components leads to a further development of the plastic properties of the paste, which occurs due to decreasing the share of fast elastic deformations in the total balance (Fig. 1) and also by a certain increase in elasticity (Table 1). One should note as well the growing strength of the coagulation structure and the flow index decreasing nearly by half. The latter can be regarded as positive consequences [6] of joint milling.

We attribute the high plasticity and the low values of the paste relaxation period primarily to the fact that its components are capable of easily binding great quantities of water from the dispersion medium, which easily penetrates the interlayer spaces of the crystal lattices of the solid phase. This leads to swelling, and the paste become “fat”. The use of grog additives, such as quartz or corundum in this case is undesirable for the reasons specified in [3, 5].

Excessive plasticity and an insufficiently strong coagulation structure prevent molding high-quality products of a complex profile. The enhanced plasticity in extrusion produces such defects as cords or “dragon teeth” depending on the extrusion velocity, whereas the low strength of the paste structure significantly complicates the subsequent operations (cutting, drying), since molded products deform easily.

A paste prepared from a mixture of hydroxides (II) subjected to separate milling typically has fast elastic deformations prevailing in the total balance and belongs to structural-mechanical type 3 (Fig. 1). The use of joint dispersion increases the plasticity by decreasing the share of fast elastic deformations, so that the paste belongs to the structural-mechanical type 4. It should be noted that, similarly to the first case, joint milling leads to the development of plastic properties of the paste, while the elasticity remains approximately at the same level. Furthermore, the relaxation period decreases, the strength of the coagulation structure increases, and the flow index decreases (Table 1). However, the paste prepared from mixture II has an extremely low strength of the coagulation structure (1.0 – 1.8 MW/m^3), which prevents molding any articles. Under the effect of a load applied in extrusion to squeeze the paste through the die, it becomes perceptibly thin-

TABLE 1

Sample*	Structural-mechanical properties			Flow properties			
	plasticity, 10^{-6} sec^{-1}	elasticity	relaxation period, sec	total flow power, MW/m^3	power on structure destruction, MW/m^3	effective viscosity, $\text{Pa} \cdot \text{sec}$	flow index
1	2.4	0.4	600	4.2	2.5	65	0.66
2	3.6	0.5	300	6.1	3.9	25	0.28
3	0.4	0.2	2100	3.3	1.0	2	0.87
4	0.7	0.3	800	4.0	1.8	9	0.71
5	0.6	0.3	5805	4.5	2.6	60	0.62
6	3.5	0.4	1855	14.3	8.4	94	0.34
7	9.5	0.3	1325	20.2	15.8	110	0.28
8	9.8	0.3	1285	20.8	16.1	114	0.27

* Sample numbers corresponds to the numbers indicates in Fig. 1.

ner due to the virtually complete destruction of the structure and literally spills from the molding nozzle.

Considering the identical effect of the milling method on the structural-mechanical and flow properties of pastes based on mixtures I and II, the following should be noted. At the stage of joint dispersion, solid-phase reactions between the components and mixing at the cluster level take place [3]. Since these processes primarily occur on the surface of particles, this obviously modifies the structure of the solvate layer, which, in turn, has an essential effect on the type of interaction between the particles and, accordingly, on the interaction between the particles and on the nature of the coagulation bonds responsible for the flows properties of the disperse system. Another common feature of mixtures I and II is the fact that all their components contain crystallization water that can easily enough be released under mechanical loading in a mill [1]. Thus, an identical impact on these mixtures produces the similar effects on the modification of the structural-mechanical and flow properties of pastes based on these mixtures.

Let us consider the properties of the paste prepared from cordierite (mixture III). As cordierite is synthesized at a temperature of 1200°C [3], it has low chemical activity, similarly any compound subjected to high-temperature treatment. It is known that for a suspension to form coagulation bonds, the dispersion medium has to react with the solid phase surface. Our earlier research of the molding properties of pastes based on α - Al_2O_3 and aluminum titanate [3, 7] (which are produced by high-temperature firing as well) demonstrated that preliminary milling of components in the presence of dry surfactant additives is a powerful instrument of controlling the structural-mechanical and flow properties of pastes based on the specified compounds. Since the pastes based on cordierite are not moldable without additives (due to a low chemical activity of cordierite, coagulation bonds are virtually never formed contact with water), we have used joint dispersion of cordierite in the presence of dry PVA to obtain pastes suitable for extrusion.

The experimental data show (Fig. 1 and Table 1) that plastic properties evolve in the pastes with a growing PVA content, while the elasticity values remain at approximately the same level. A mixture of structural-mechanical type 1 (1% PVA) first transforms into type 2 (3% PVA). On a further increase in PVA content to 5 and 7%, plastic deformations start to prevail in the total deformation balance and the pastes are classified as structural-mechanical type 5, while staying close to the center of the diagram. This indicates that the part of the fast and slow elastic deformations remains perceptible. The evolution of the plastic properties of pastes is accompanied by a decrease in the relaxation period to less than one-fourth, a five-time increase in the strength of the coagulation structure, and a decrease in the flow index from 0.62 to 0.27–0.28. According to the conclusions in [6, 7], these trends have a positive effect. Indeed, it is easy to form products of a rather complex profile from a paste with 3%

PVA, and when the PVA content increases to 5% and more, it becomes possible to extrude virtually any shapes, including blocks with a cellular structure.

It is notable that the most perceptible effect on modifying paste properties is observed upon the PVA content in the mixture growing up to 5%. Thus, an increase in the PVA content from 1 to 3% causes a triple increase in the strength of the coagulation structure. A further increase of PVA in the paste to 5% increases the strength of the coagulation structure less than twice, and for 7% PVA an increase in this parameters is virtually imperceptible (Table 1). The plasticity values change with an increasing concentration of PVA in the similar way. The relaxation period and the flow index of pastes decrease with an increasing PVA content, and the most significant changes as well are observed while the PVA content in the paste grows up to 5%.

We attribute these phenomena to the fact that the content of approximately 5% PVA is the PBA level, at which the formation of the solvate shell around the cordierite particle ends, i.e., the shell becomes saturated with respect to PVA molecules. As the content of the surfactant in the mixture increases further, excessive PVA molecules virtually do not participate in the surface – liquid phase structure-formation processes and only modify the properties of the dispersion medium. This is supported by the above considered experimental data. Thus, within the range of a low (up to 3%) PVA content the solvate layer is just being formed, consequently, even an significant variation in the PVA content in the mixture perceptibly changes the structural-mechanical and flow properties of the pastes dependent on the coagulation bonds (formed with a direct participation of solvate layers) between particles. For a relatively high PVA content (above 3%) the formation of a solvate shell is virtually completed, and the effect of PVA content variations is not so significant.

When molding articles of a complex profile, it is essential not only to obtain a required shape of the extrudate, but also to preserve it at the subsequent stages of drying and calcination. We earlier demonstrated [3] that articles molded from initial components (mixtures I and II in the present study) have a linear shrinkage of 15–20% in the drying and calcination stages, which leads to the formation of cracks up to the destruction of the sample. Linear shrinkage in drying and calcination of samples molded from cordierite does not exceed 5%, which is quite acceptable.

Let us consider the variations of the volume of pores and the mechanical strength of samples molded from cordierite with 3–5% PVA additive (Fig. 2).

As the calcination temperature grows to about 600°C, the volume of open pores increases, while the volume of the sealed pores decreases. An increased porosity of material in this temperature range is accompanied by decreasing the mechanical strength of the sample. The pore volume increases primarily due to the removal of the adsorption moisture from the system, and then PVA burning out. The strength of the samples in the considered temperature interval primarily de-

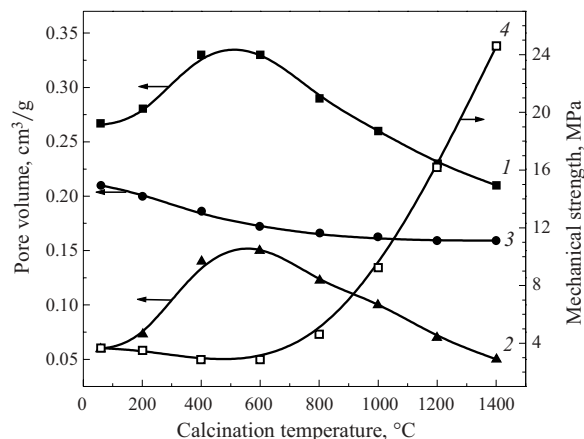


Fig. 2. Dependence of the pore volume [1) total, 2) open, 3) sealed] and strength (4) of cordierite samples on calcination temperature.

depends on the number of contacts between the solid phase particles, which decreases with increasing porosity.

A further increase in the firing temperature (over 600°C) decreases the porosity of the sample by decreasing the volume of open pores. The strength of the sample in this case sharply grows. This shows that the strength of the sample at high temperatures is determined not by a number of contacts between the particles, but by their individual strength.

It follows from the above data (Fig. 2) that rather high strength (approximately 10 MPa) is reached already at 1000°C. This high mechanical strength value at rather low firing temperatures is primarily related to the effect of mechanochemical activation of cordierite milled in the presence of the surfactant additive. The PVA molecules sorbed on particles in milling decrease their surface energy, which facilitates the accumulation of excessive energy in the form of the energy of crystal structure defects (point, linear, or planar). The excessive energy of these defects in calcination becomes released, and crystalline bonds are formed between the particles. An increased activity of the defects induced in

the course of dispersion in the presence of PVA contributes to the formation of crystallization contacts at lower (1000–1200°C) temperatures.

REFERENCES

1. E. G. Avvakumov and A. A. Gusev, *Cordierite As a Promising Ceramic Material* [in Russian], Izd-vo SO RAN, Novosibirsk (1999).
2. E. G. Avvakumov, E. T. Devyatkina, N. V. Kosova, et al., "A new mechanochemical method for preparing cordierite and cordierite-based carrier," *Kinetika Kataliz*, **39**(5), 722–725 (1998).
3. V. Yu. Prokof'ev, A. V. Kunin, A. P. Il'in, et al., "The use of mechanochemical methods for the synthesis of cordierite catalyst carriers," *Zh. Prikl. Khim.*, **70**, Issue 10, 1655–1659 (1997).
4. A. F. Bessonov and E. V. Bessonova, "Kinetics and mechanism of phase formation in heating a mixture of MgO, Al₂O₃, and SiO₂," *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, **20**(1), 92–96 (1984).
5. V. E. Morozkova, G. R. Karagedov, and A. S. Berger, "The effect of mechanical activation on the synthesis and sintering of cordierite," *Sib. Khim. Zh.*, Issue 1, 115–118 (1993).
6. V. Yu. Prokof'ev, A. P. Il'in, Yu. G. Shirokov, and É. N. Yurchenko, "The selection of optimum properties of molding mixtures for extrusion of block carriers and catalysts with a cellular structure," *Zh. Prikl. Khim.*, **68**, Issue 4, 613–618 (1995).
7. V. Yu. Prokof'ev, A. P. Il'in, Yu. G. Shirokov, et al., "The impact of relaxation effects on the process of extrusion of carriers and catalysts," *Zh. Prikl. Khim.*, **69**, Issue 10, 1685–1690 (1996).
8. V. Yu. Prokof'ev and A. P. Il'in, "Structure formation and controlling properties of molding mixtures for extrusion," *Izv. Vuzov, Ser. Khimiya Khim. Tekhnol.*, **44**, Issue 2, 72–77 (2001).
9. É. N. Yurchenko, V. Yu. Prokof'ev, A. P. Il'in, and Yu. G. Shirokov, "Control of structural-mechanical and flow properties of molding mixtures based on titanium dioxide," *Zh. Prikl. Khim.*, **68**, Issue 4, 607–612 (1995).
10. N. N. Kruglitskii, *Principles of Physicochemical Mechanics, Part I* [in Russian], Kiev, Vishcha Shkola (1975).
11. E. D. Shchukin, A. I. Bessonov, and S. A. Paranskii, *Mechanical Tests of Catalysts and Sorbents* [in Russian], Nauka, Moscow (1971).